Electronic and magnetic properties of two-dimensional Li_3N

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Using first-principles plane-wave calculations study of electronic and magnetic properties of hypothetical two-dimensional structure of Li_2N compound have been conducted. Calculations show, that electronic properties of this this structure can be inflenced by hydrogenation, which may change the system from wide-gap semiconductor to metal. Also, non-zero magnetic moment, equal to 1 μ_B can be generated by intruduction of H vacanies in hydrogenated structure.

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I. INTRODUCTION

Since its discovery in 2004 graphene [1] draws much attention because of unique features of this two-dimensional system. Graphene is composed of a sp^2-bonded carbon atoms forming honeycomb structure. It became famous for its very interesting electronic structure with characteristic, linear energy dispersion near K point of Brillouin zone and many other features [3].
Shortly after, experimental techniques allowed fabrication of other new two-dimensional materials, like BN and MoS_2 honeycomb structures [2]. The discovery of such stable two-dimensional materials triggered search for similar structures made from different compounds. Up to now many of these hypothetical structures constructed from silanene (2D Si) and germanene (2D Ge) [4, 5], III-V compounds [6], SiC [7] or ZnO [8] have been studied theoretically. Also, calculations show [9], that graphene-like type of structure is not the only one possible for two-dimensional material. This new class of boron sheets, composed of triangular and hexagonal motifs can be stabilized by interplay of three- and two-center bonding scheme [10]. Another example of triangular sheet could be found in already known material, which is Li_3N in its α phase.
Li_3N is a bulk material known to be a fast ion conductor [32]. Li_3N is also known as a candidate for hydrogen storage material due its high theoretical H_2 capacity [13]. Bulk Li_3N crystallizes in hexagonal structure which is characterized by $P6/mmm$ symmetry group, each nitrogen atom is surrounded by eight lithium atoms. It has layered structure, one layer is Li_2N and the other is of Li atoms only. Previous theoretical studies confirm ionic nature of bonding in this compound [11, 12]. Since N-containing layer is rather weakly bound with two Li-only layers, it would be interesting to study electronic properties of such two-dimensional structure ($2DLi_2N$) - Fig 1a. Since this structure would have N atoms with dangling bonds, it would give opportunity to study influence of different atoms addition on them. For example addition of hydrogen atoms in case of graphene resulted in new material which is graphane [15].
Graphene and other nano-scale materials are recognized as future building blocks of new electronics technologies [16], including spintronics [17]. In the case of low (one- and two-) dimensional structures problem arises because of famous Mermin-Wagner theorem [18], which prevents ferro- or antiferromagnetic order to occur in finite temperatures, which is essential for practical application. This started the theoretical and experimental search for magnetism in graphene and other two-dimensional structures. One of the most promising directions is emergence of magnetism in such structures as an effect of presence of local defects [19]. According to works of Palacios et al. [20] and, independently, of Yazyev [21] single-atom defects can induce ferromagnetism in graphene based materials. In both cases, the magnetic order arises as an effect of presence of single-atom defects in combination with a sublattice discriminating mechanism. In the case of $2DLi_2N$role of such defect could play non-hydrogenated N atom in hydrogenated structure. It would be then instructive to check influence of hydrogenation level on magnetic moment of the structure.
In this paper electronic and magnetic structure of pure and hydrogenated $2DLi_2N$ have been analyzed by means of *ab-initio* calculations.

II. COMPUTATIONAL DETAILS

To investigate electronic and magnetic properties of two-dimensional Li_3N structures a series of *ab-initio* calculations have been conducted with use of DFT VASP code [25, 26] with PAW potentials [27]. For both spin-unpolarized and spin-polarized cases exchange-correlation potential has been approximated by generalized gradient approximation (GGA) using PW91 functional [28]. Kinetic energy cutoff of 500 eV for plane-wave basis set has been used. In all cases for self-consistent structure optimizations, the Brillouin zone (BZ) was sampled by $20 \times 20 \times 1$ special k points. All structures have been optimized for both, spin-unpolarized and spin-polarized cases unless Feynman-Hellman forces acting on each atom become smaller than 10^{-4} eV/Å. A vacuum spacing of 12 Å was applied to hinder the interactions between $2DLi_2N$monolayers in ad-

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jacent cells. (dop. kiedy supercell i jak liczone magn.) Bandstructure and density of states (DoS) calculations have been confirmed by use of WIEN2k code [29] which implements the full-potential linearized augmented plane wave (FLAPW) method [30]. In this case for exchange and correlation generalized gradient approximation was used in the Perdew-Burke-Ernzerhoff (PBE) parameterization [31].

III. RESULTS - ELECTRONIC STRUCTURE

To study electronic properties of 2DLi$_2$N, at first comparison has been made with bulk material. For both cases lattice constants have been determined by total energy calculations and are found to be equal to 3.65 Å for bulk (experimental value 3.63 Å) and 3.57 Å for 2DLi$_2$N. In agreement with [14] bulk Li$_3$N is a semiconductor with non-direct bandgap equal to 1.15 eV between A (valence band) and Γ (conduction band) points. In contradiction to this, 2DLi$_2$N has metallic nature.

Two-dimensional structure is rather weakly bound - binding energy (defined as $E_b = E_{at} - E_{sheet}$ where E_{at} is the energy of isolated atom(s) and E_{sheet} is the total energy of two-dimensional structure) is equal to 10.36 eV, while binding energy of bulk structure is equal to 14.25 eV. Also, two dimensional sheet would have N atoms with dangling bonds, such structure would be then rather unstable with respect to foreign atoms addition. Graphane case suggests that it would be instructive to examine influenece of hydrogenation on electronic structure in such cases as well as addition of lithium atoms.

The nature of Li-N bond is ionic, as it can be seen from Fig. 2 showing charge density projected on [110] plane. Since every bond has both ionic and covalent character the level of ionicity can be estimated using difference between electronegativities of bonded atoms [33]. In the case of Li-N bond this difference equal to 2 suggests, that the bond is about 65% ionic and 35%covalent. This fact together with rather large lattice constant suggest that the structure of two-dimensional 2DLi$_2$N can be low-buckled (LB) rather than plane (PL), according to puckering mechanism described in [6]. To check this the series of calculations has been done, each with different distance in z direction between Li atoms and the plane on which N atoms lie (Δz). The structure with minimal energy has been then optimized. Calculations show, that the buckled structure with Δz = X lies 0.54 eV lower that the plane, which means that indeed the puckering mechanism stabilizes the structure. Both, plane and low-buckled structures can be seen on Fig 1.

Four structures have been then studied in two conformations, plane and low-buckled — two (PL and LB) with single H atom attached on top of each N atom (2DLi$_2$N+H), two with two H atoms attached on both sides of N (2DLi$_2$N+2H), two with single Li atom attached on top of each N atom (2DLi$_2$N+Li), and two with two Li atoms attached on both sides of N (2DLi$_2$N+2Li).

Calculated binding energies, hydrogen-addition energies, lithium-addition energies, and structure parameters are shown in Tab. 1 (plane structure) and Tab. 2 (low-buckled structure). In Tab. 1 d$_{N-H}$ is the distance between N and passivated H atoms, d$_{N-Li}$ is the distance between N and passivated Li atoms, and Δz is distance in the z direction between Li atoms and the plane on which N atoms lie. In tab. 2 E$_t$ is total energy of the structure with reference to plane structure. As can be seen, in all cases low-buckled structure is lower in energy, from 0.01 eV for 2DLi$_2$N+2Li to 1.08 eV for 2DLi$_2$N+2H. So, from now on, all properties are referred to LB structure, unless stated otherwise.

Binding energy of 2DLi$_2$N+H, equal to 16.27 eV, is comparable to binding energy of bulk structure (both have the same number of atoms in the unit cell), which suggests that H-passivated two-dimensional structure would be no less stable than the bulk. Addition energies are defined as E_{add} = E_{tot}(layer+addatom) − E_{tot}(layer) − E_{tot}(addatom). High value of addition energy for single H atom equal to 5.55 eV suggests, that hydrogen addition may stabilize the structure, making it more bound. Addition of second H atom to already H-passivated structure requires only 1.44 eV, which means that 2DLi$_2$N+2H structure is less stable than 2DLi$_2$N+H. Addition energy of 2.11 eV for single Li atom on pure layer is almost equal to addition energy for single Li atom on Li-passivated structure (1.74 eV), but such structures are less bound that H-passivated cases.

MW →

The electronic structure of a single-layer 2DLi$_2$N (not taking into account the Fermi level) exhibits typical structure of a semiconductor, with valence and conduction bands separated by a band gap of 4 eV. Its metallic character is purely due to the position of Fermi level which is lowered by -2 eV from the middle of the band gap to the upper part of the valence band. This may be explained by a large contribution to the density of states of the valence band coming from the p-electrons from N atoms. The conduction band of a single-layer 2DLi$_2$N originates mainly from the density of states of p-electrons of lithium.

The relative positions of bands in band structure of 2DLi$_2$N+H with single H atoms added, remain unchanged with respect to 2DLi$_2$N+H with the exception of a single nitrogen p-electrons band, which is lowered by 2 eV. The Fermi level is rised by 2 eV from the conduction band to the middle of the band gap, and therefore 2DLi$_2$N+H is semiconductor. The rising of the Fermi level is caused by an increased contribution to the density of states from lithium p-electrons (see Fig. 2e). The contributions of s-states originating from additional hydrogen is insignificant.

The same effect can be observed when the second H atom is added to the 2DLi$_2$N+H layer. The Fermi level is rised again by 2 eV with respect to the position of

bands, and is placed at the bottom of the conduction band. Therefore $2DLi_2N+2H$ is again metallic.

We can summarize the effect of H atom addition: each H atoms rises the Fermi level by 2 eV and the band structure remains unchanged.

Addition of lithium atoms to the single-layer $2DLi_2N$ leads to quite different effects. The band structure of $2DLi_2N+Li$ is purely metallic with no band gap. The energy band of p-electrons for additional litium atom connects the conduction band of the original $2DLi_2N$ band structure at K and M points of the Brillouine zone with the valence band at Γ point, effectively nullyfing the energy gap. There exists non-zero density of states of p-electrons for additional litium atom directly at the Fermi level. The Fermi level is practicaly unchanged with respect to the band structure and remains at the top of the conduction band of the original $2DLi_2N$ band structure.

Addition of second lithium atom repeats the effects of the first one. There appears a new steep band of lithium p-electrons and the resulting structure remains metallic. The Fermi level is shifted up by about 1 eV with respect to the band structure, however is does not influence the metallic character of the compound.

We can summarize the effect of Li atom additions: each Li atoms adds an energy band directly across the energy gap of the the original $2DLi_2N$ band structure.

MW ←

IV. CONCLUSIONS

Ab-initio calculations have been conducted for hypothetical two-dimensional material $2DLi_2N$ to investigate electronic and magnetic properties. Calculations show, that structure is much more stable when dangling bonds of nitrogen atoms are functionalized with hydrogen atoms. This hydrogenation has very strong influence on on bandstructure, changing it from wide-gap semiconductor to metal.

Magnetic properties are also interesting. In analogy to graphene and other two-dimensional materials it is possible to generate non-zero magnetic moment by introduction of distorsion. In the case of $2DLi_2N$ the distorsion would be a two-hydrogen or hydrohen-lithium vacancy around the same nitrogen atom. This generates magnetic moment of 1 μ_B. Since bulk Li_3N material has ususally 1-2% Li vacancies in Li_2N layers [14] such two-dimensional hydrogenated sheet would be almost naturally magnetic. These results may give a hint for experimentalists seeking for two-dimensional (magnetic) materials, which would be interesitng addition to growing family of two-dimensional materials.

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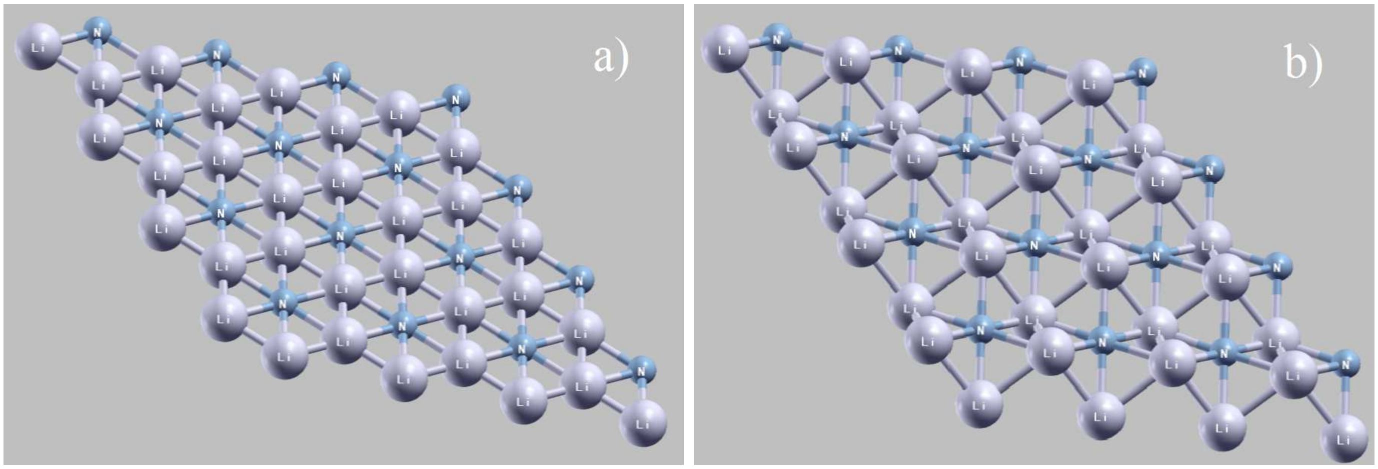


FIG. 1. Atomic structure of plane (a) vs. low-buckled (b) $2DLi_2N$ (color online)

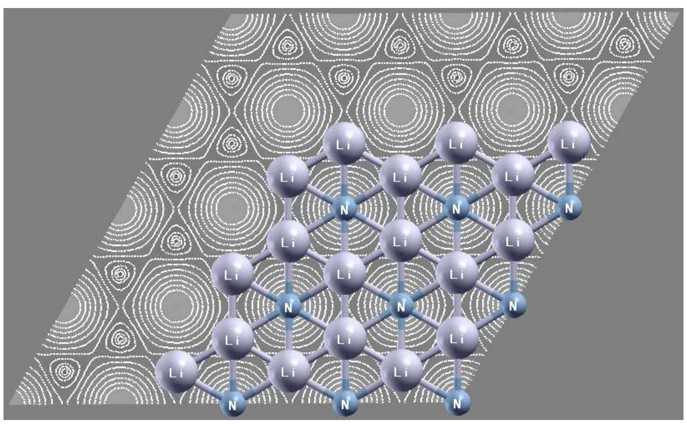


FIG. 2. Valence charge density of (?) (color online)

	$2DLi_2N$	$2DLi_2N$+H	$2DLi_2N$+2H	$2DLi_2N$+Li	$2DLi_2N$+2Li
E_b (eV)	10.36	15.98	16.88	13.04	15.37
E_{add} (eV)	-	5.80	0.90	2.86	2.29
d_{N-H} (Å)	-	1.046	1.157	-	-
d_{N-Li} (Å)	-	-	-	1.88	1.99
Δz_{N-Li} (Å)	0.0	0.129	0.0	0.187	0.0

TABLE I. Comparison of binding and addition energies and structure parameters of two-dimensional plane $2DLi_2N$.

	$2DLi_2N$	$2DLi_2N$+H	$2DLi_2N$+2H	$2DLi_2N$+Li	$2DLi_2N$+2Li
E_t (eV)	0.54	0.29	1.08	0.21	0.01
E_{add} (eV)	-	5.55	1.44	2.11	1.74
d_{N-H} (Å)	-	1.05	1.21	-	-
d_{N-Li} (Å)	-	-	-	1.91	2.00
Δz_{N-Li} (Å)	0.49	0.60	0.84	0.30	0.22

TABLE II. Comparison of total energy (with reference to plane structure) and structure parameters of two-dimensional low-buckled $2DLi_2N$.

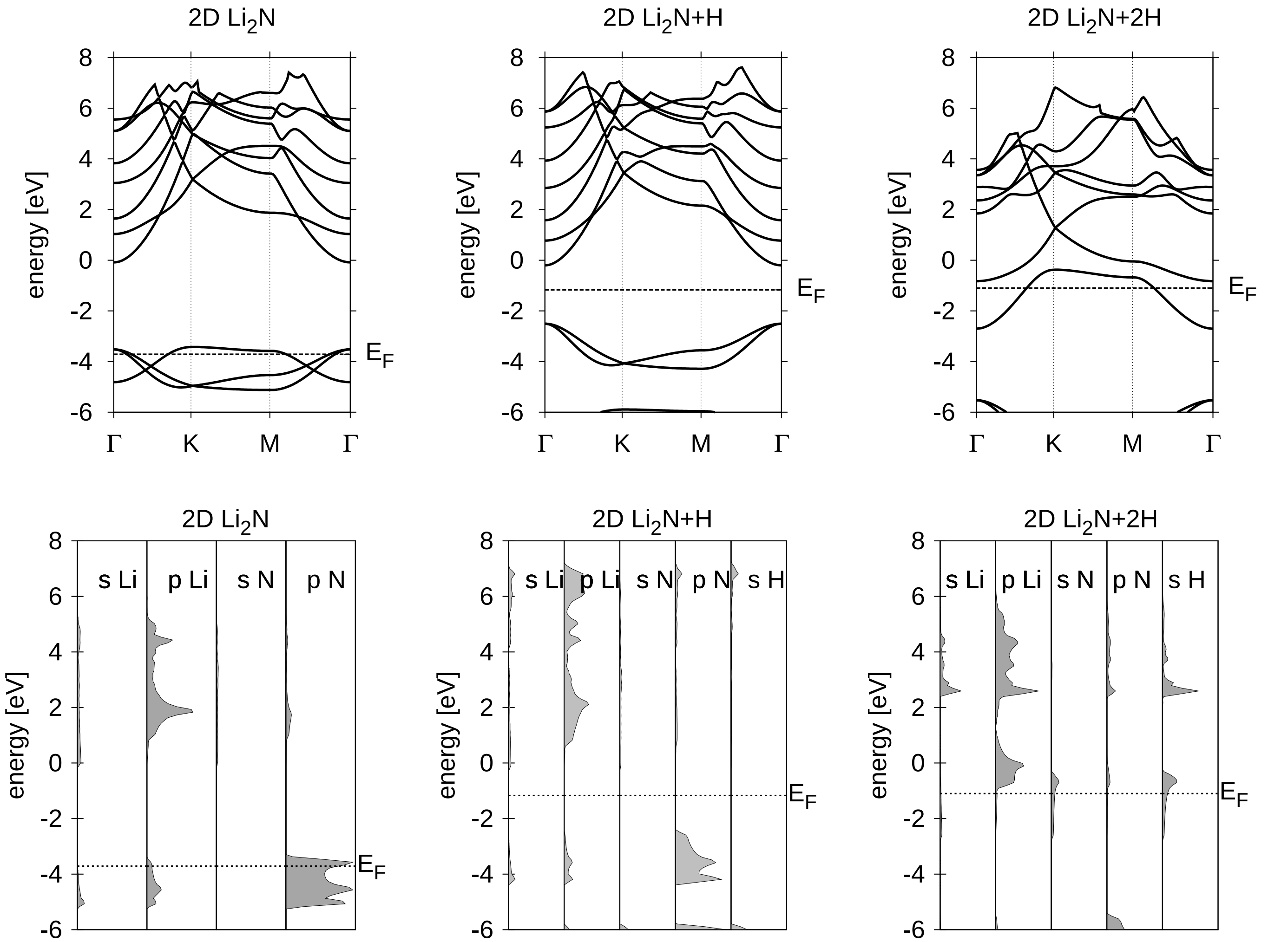


FIG. 3. Bandstructures and partial density of states for PL $2\mathrm{DLi_2N}$, $2\mathrm{DLi_2N}$+H and $2\mathrm{DLi_2N}$+2H. Details in text.

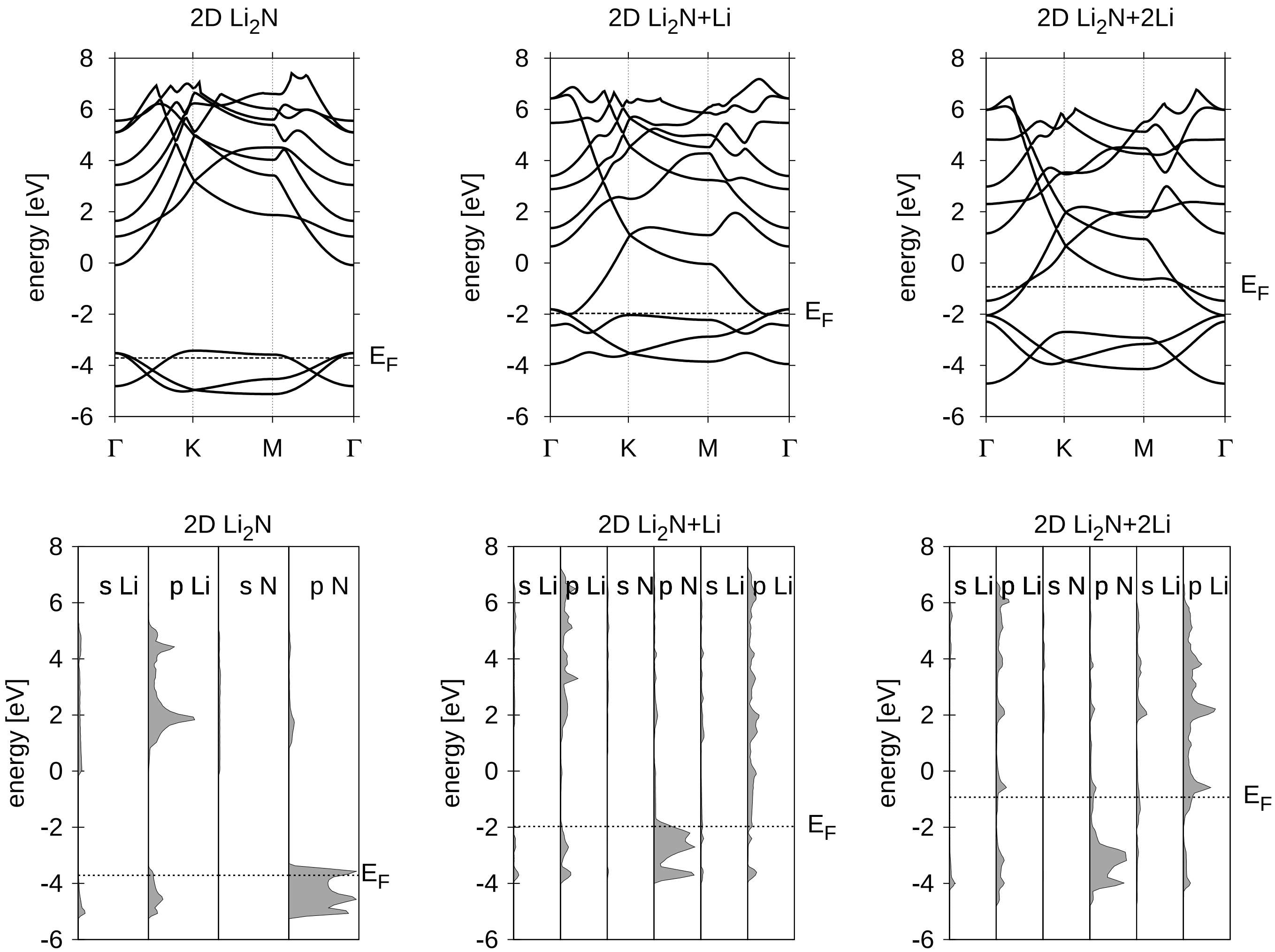


FIG. 4. Bandstructures and partial density of states for PL $2DLi_2N$, $2DLi_2N$+Li and $2DLi_2N$+2Li. Details in text.

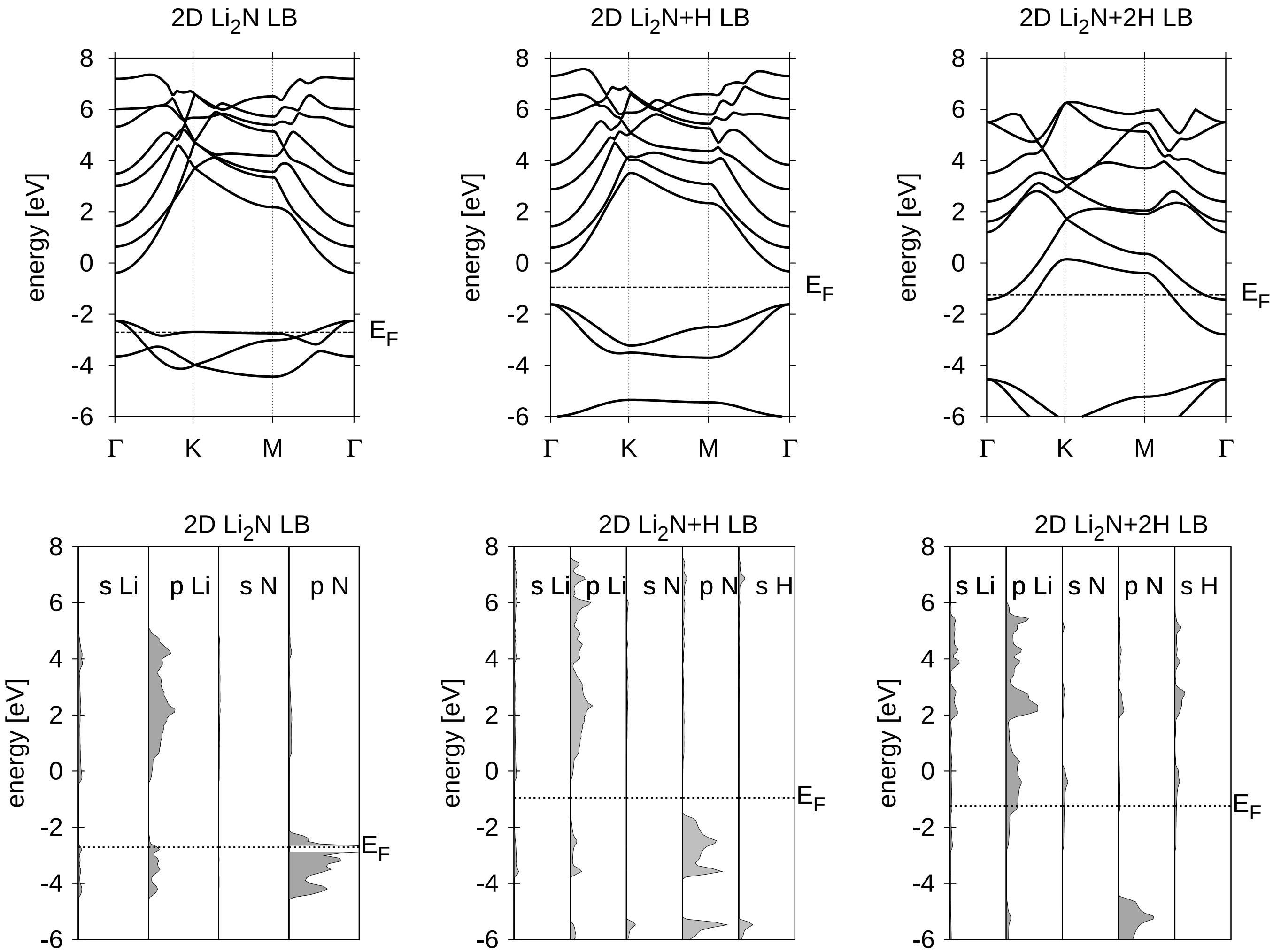


FIG. 5. Bandstructures and partial density of states for LB $2DLi_2N$, $2DLi_2N$+H and $2DLi_2N$+2H. Details in text.

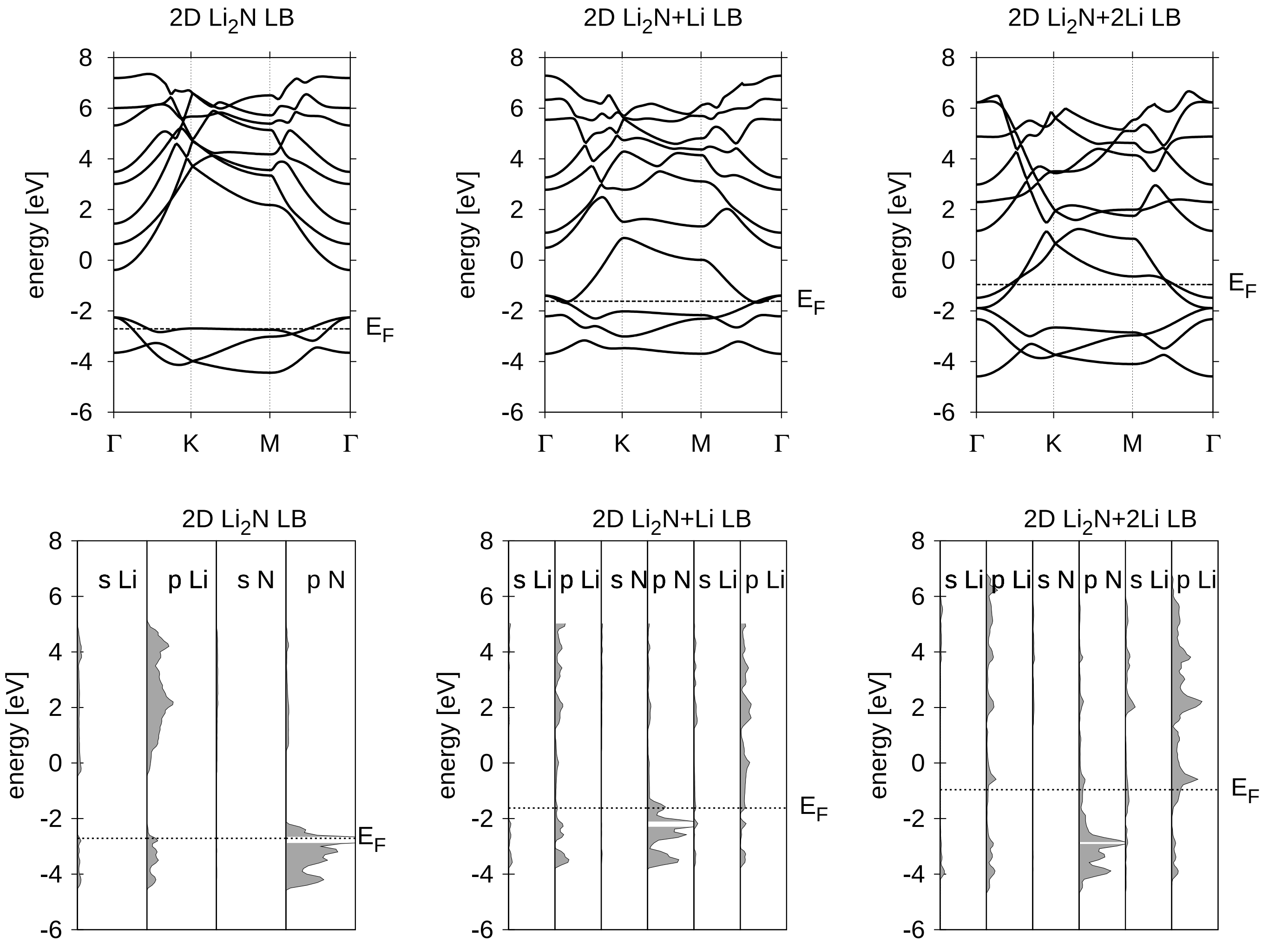
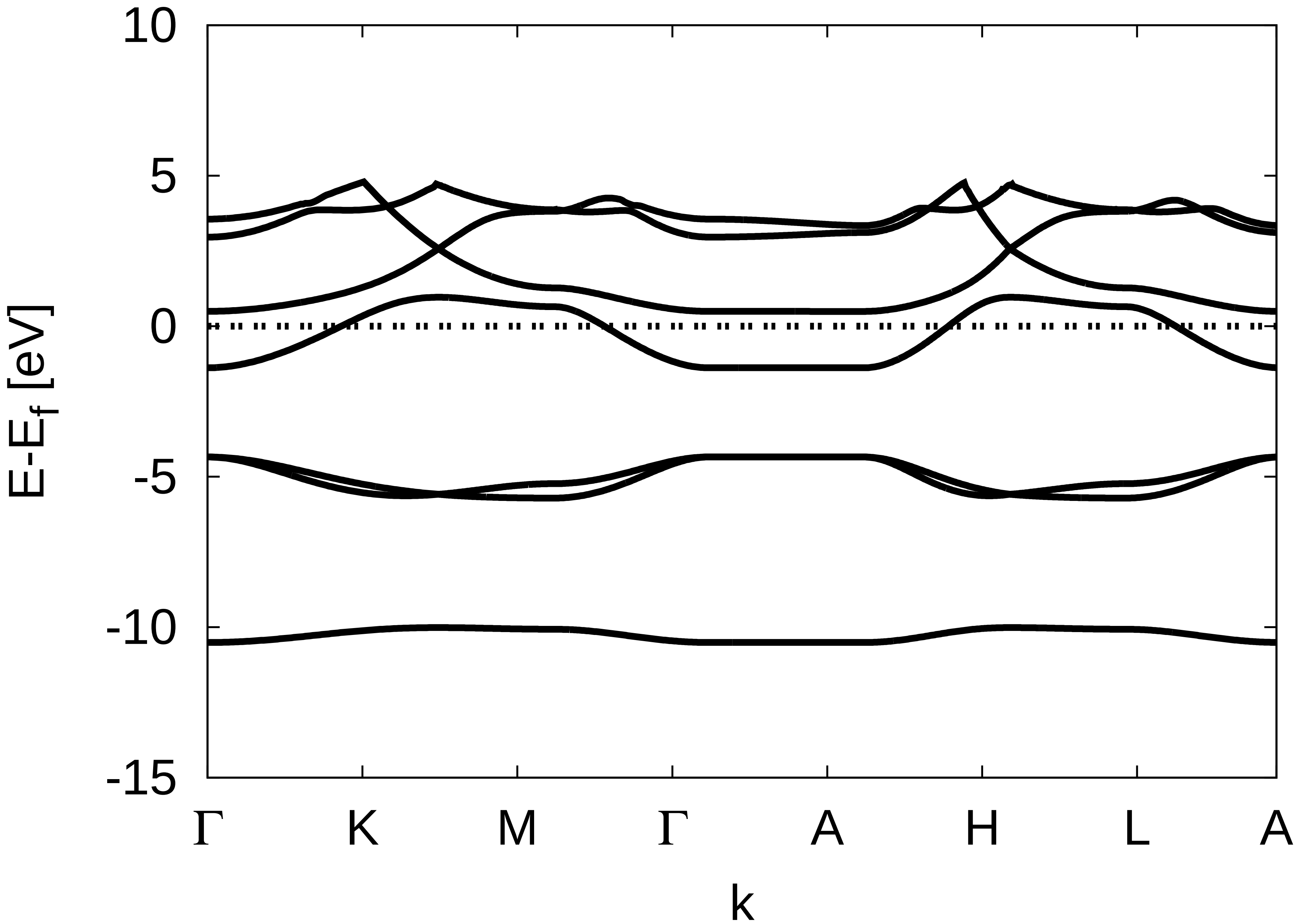


FIG. 6. Bandstructures and partial density of states for LB $2DLi_2N$, $2DLi_2N$+Li and $2DLi_2N$+2Li. Details in text.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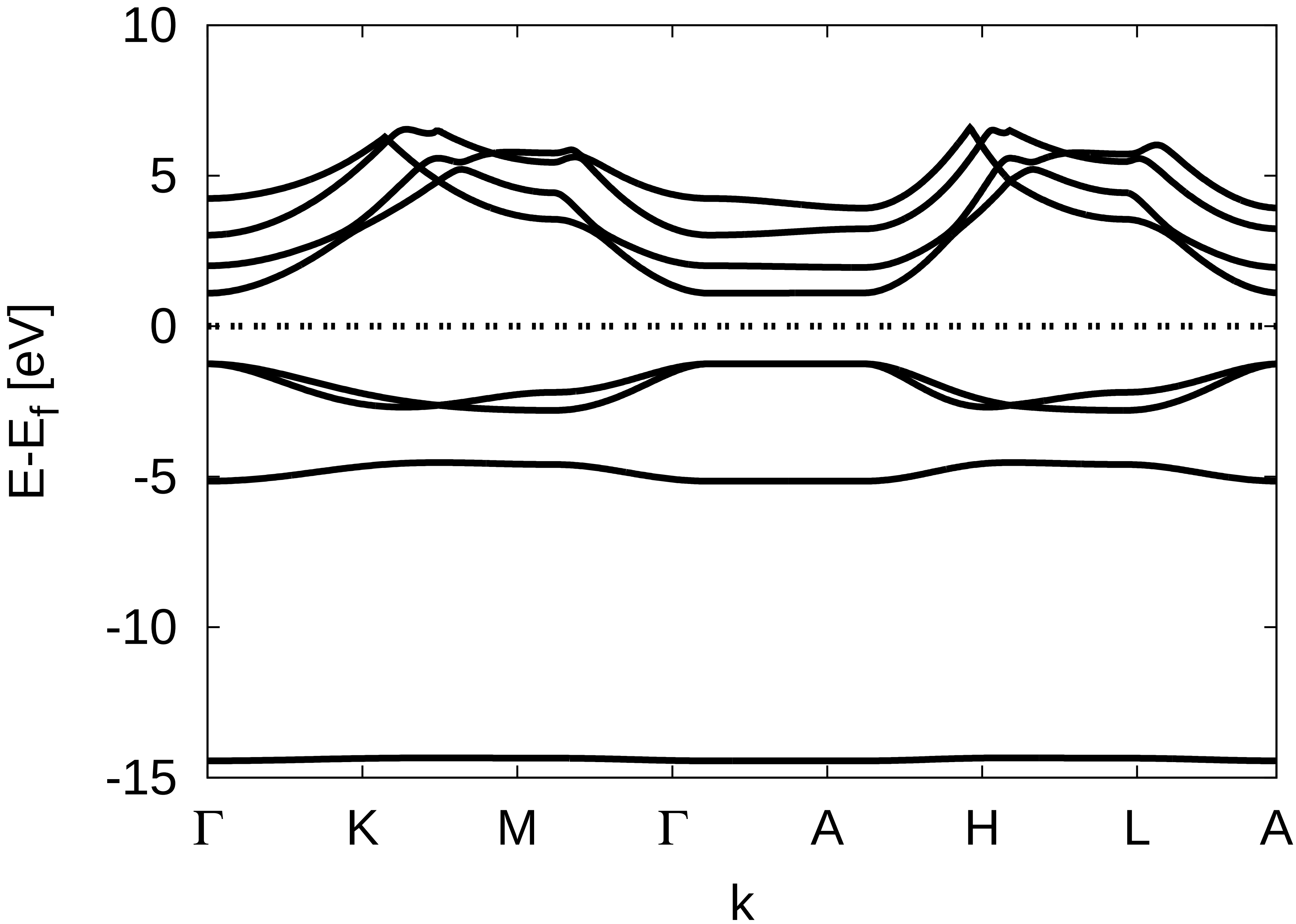

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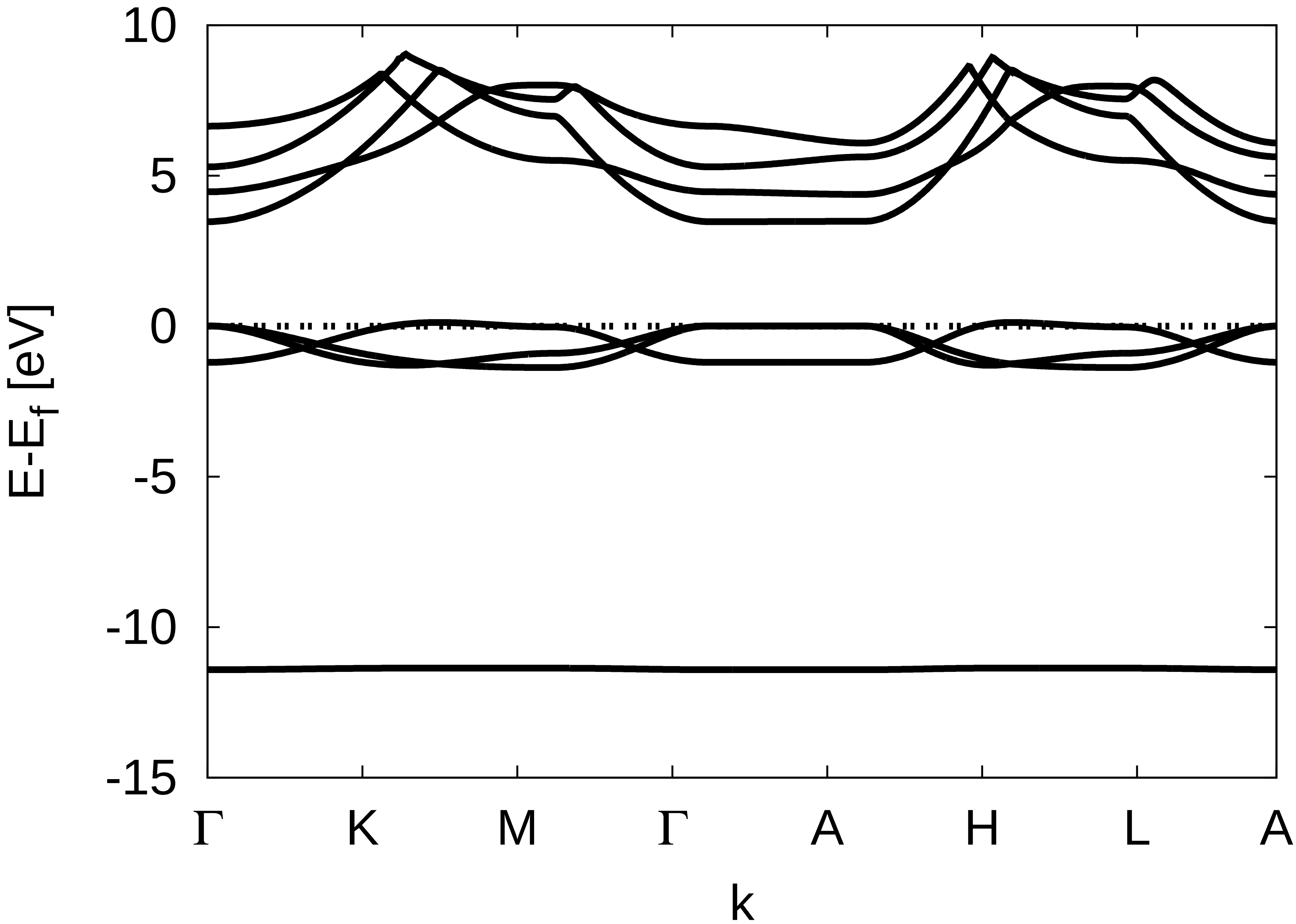
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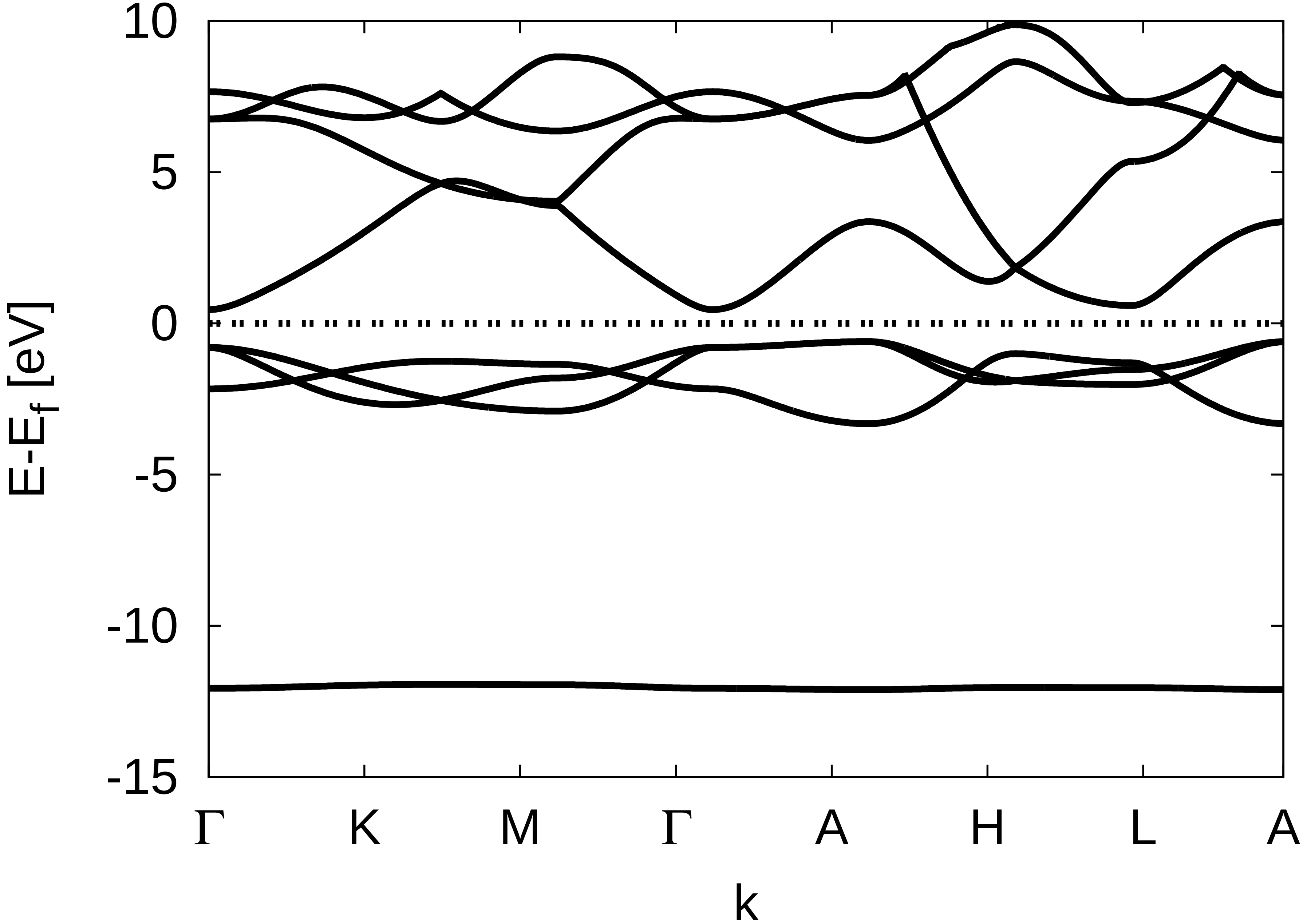

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E-E$_f$ [eV]
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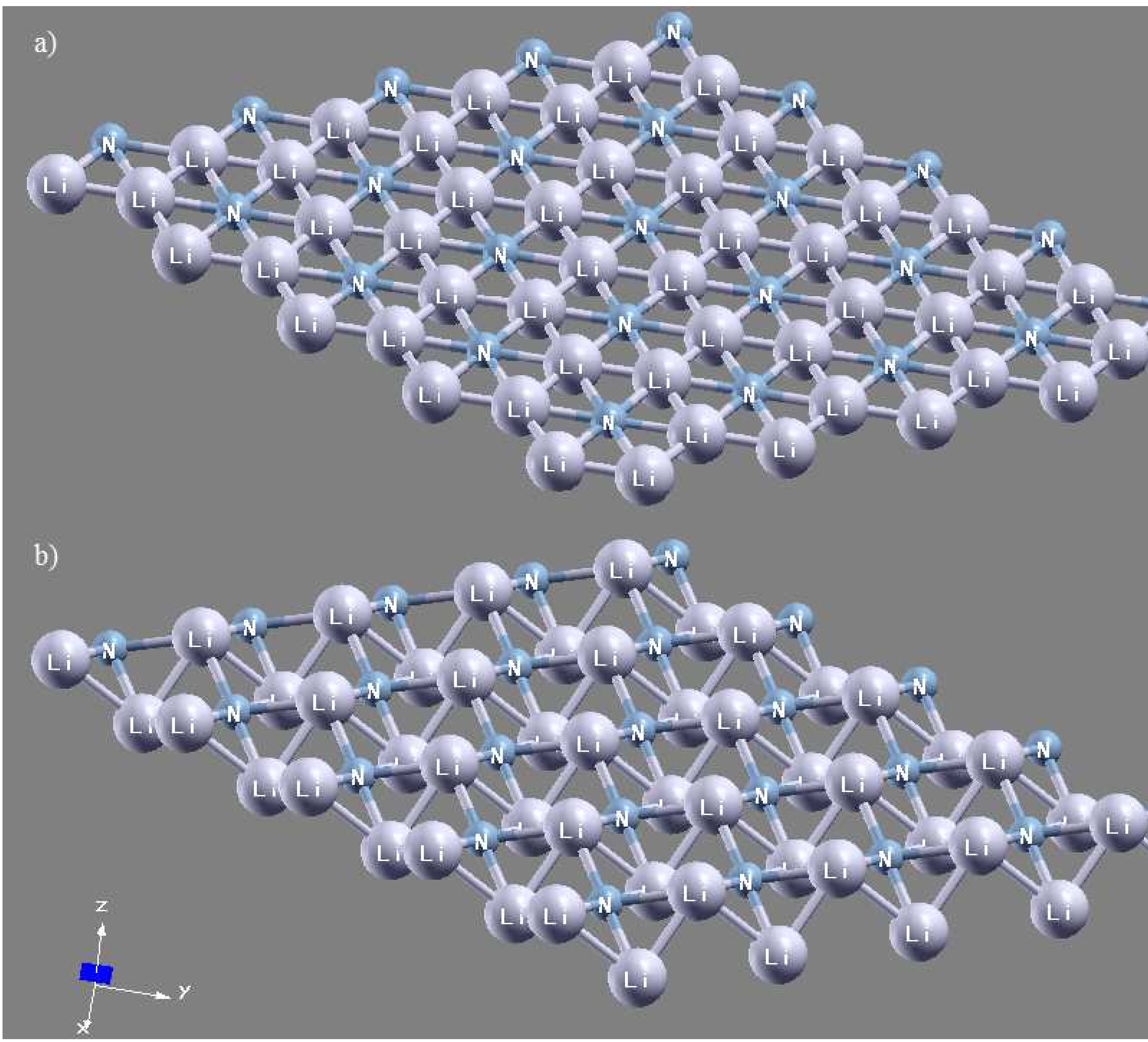

a)
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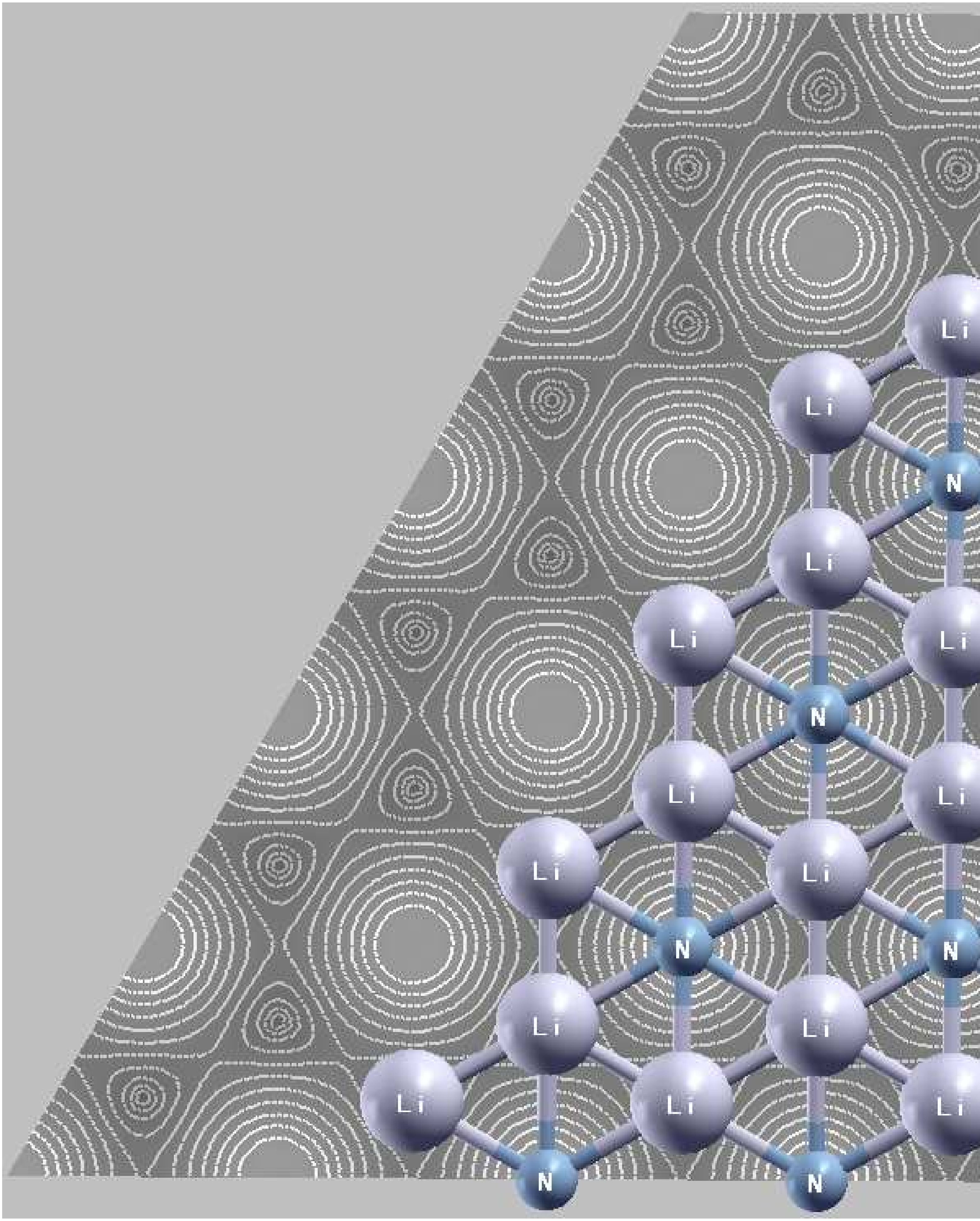
Li
N